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## III.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.*

### 1. ON CERTAIN SUBSTITUTED ACRYLIC AND PROPIONIC ACIDS.

BY C. F. MABERY AND F. C. ROBINSON.

Presented January 10th, 1883.

$\beta$-DIBROMACRYLIC acid, unlike the isomeric $\alpha$-acid, will not unite with bromine at ordinary temperatures. After standing twelve days, a solution of the acid with bromine in chloroform was not bleached, and by slow evaporation of the solution crystals were deposited which melted at 86°, the melting-point of dibromacrylic acid. At 100° the addition of bromine was easily accomplished. When pure dibromacrylic acid was heated in a closed tube with undiluted bromine in slight excess over the calculated amount for one or two hours, tetrabrompropionic acid was formed in nearly the theoretical quantity. The excess of bromine was removed by evaporation from the crude product, which was purified by pressure in filter-paper and crystallization from carbonic disulphide and chloroform. From a concentrated solution in carbonic disulphide it crystallizes by slow evaporation in oblique prisms. It is somewhat soluble in hot water, from which it separates at first as an oil; but on further cooling it crystallizes in thick prisms. On boiling an aqueous solution of the acid, it is rapidly decomposed, imparting a milky appearance to the solution, probably from the formation of tribromethylen. Melting point 118°–120°. Its composition was determined by the following analyses.

I. 0.2149 grm. of the substance gave by Carius's method 0.4169 grm. AgBr.
II. 0.1639 grm. of the substance gave 0.3145 grm. AgBr.
III. 0.8899 grm. of the substance gave 0.2857 grm. $CO_2$ and 0.0478 grm. $H_2O$.

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* This work was done in connection with the summer course of instruction in chemistry for 1882. — C. F. M.

| | Calculated for $C_3H_2Br_4O_2$. | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| Br | 82.04 | 82.55 | 81.76 | |
| C | 9.23 | | | 8.76 |
| H | .51 | | | .60 |

The barium, calcium, and potassium salts of this acid were made and analyzed. We were unable to prepare the silver salt in a form sufficiently pure for analysis. Argentic bromide began to separate even in the dark as soon as the salt was formed.

*Baric tetrabrompropionate*, $Ba(C_3HBr_4O_2)_2 . \frac{1}{2} H_2O$? To prepare this salt, a solution of the acid was saturated with baric carbonate, filtered, and allowed to evaporate spontaneously at the ordinary temperature.

From the concentrated solution the salt crystallized in flat prisms, which were very soluble in water. In aqueous solution the salt is permanent when exposed to the air at ordinary temperatures, but it is rapidly decomposed by heat. In the following determinations of the water of crystallization, in each case the salt was dried to a constant weight in the air and then heated until constant at 80°.

I. 1.2784 grms. of the air-dried salt lost 0.0090 grm. $H_2O$ at 80°.
II. 1.0862 grms. of the air-dried salt lost 0.0081 grm. $H_2O$ at 80°.
III. 1.2403 grms. of the air-dried salt lost 0.0087 grm. $H_2O$ at 80°.

| | Calculated for $Ba(C_3HBr_4O_2)_2 . \frac{1}{2} H_2O$. | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| $H_2O$ | .96 | .7 | .7 | .75 |

1.0762 grms. of the salt dried at 80° gave 0.2747 grm. $BaSO_4$.

| | Calculated for $Ba(C_3HBr_4O_2)_2$. | Found. |
|---|---|---|
| Ba | 14.97 | 15.01 |

*Calcium tetrabrompropionate*, $Ca(C_3HBr_4O_2)_2 . H_2O$. When an aqueous solution of the acid was neutralized with calcic carbonate in the cold and evaporated at the ordinary temperature, the calcium salt separated from the concentrated solution in clusters of miscroscopic prisms, which were much less soluble in water than the corresponding barium salt. The air-dried salt contained one molecule of water of crystallization, which was given up at 80°.

I. 1.1413 grms. of the air-dried salt gave 0.0215 grm. $H_2O$ at 80°.
II. 1.1087 grms. of the air-dried salt gave 0.0205 grm. $H_2O$ at 80°.
III. 1.0948 grms. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.1895 grm. $CaSO_4$.

| | Calculated for $Ca(C_3HBr_4O_2)_2 . H_2O$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| $H_2O$ | 2.15 | 1.88 | 1.85 |

| | Calculated for $Ca(C_3HBr_4O_2)_2$. | Found. |
|---|---|---|
| Ca | 4.89 | 5.09 |

*Potassic tetrabrompropionate,* $KC_3HBr_4O_2 . 2 H_2O$. By the action of an aqueous solution of potassic carbonate on the acid a neutral solution was obtained, from which by spontaneous evaporation the potassium salt was deposited in the form of clustered needles. This salt is very soluble in water and permanent in the air at ordinary temperatures, but rapidly decomposed by heat. The air-dried salt gave up its water of crystallization over sulphuric acid.

I. 1.1571 grms. of the air-dried salt lost over $H_2SO_4$ 0.0882 grm. $H_2O$.
II. 1.1304 grms. of the air-dried salt lost over $H_2SO_4$ 0.0858 grm. $H_2O$.
III. 1.0354 grms. of the anhydrous salt gave on ignition with $H_2SO_4$ 0.2165 grm. $K_2SO_4$.

| | Calculated for $KC_3HBr_4O_2 . 2 H_2O$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| $H_2O$ | 7.76 | 7.62 | 7.59 |

| | Calculated for $KC_3HBr_4O_2$. | Found. |
|---|---|---|
| K | 9.14 | 9.39 |

When heated in aqueous solution the barium salt was easily decomposed with the separation of an oil which distilled readily with steam. Since tribromethylen was the only substituted hydrocarbon that could be derived from tetrabrompropionic acid under these conditions, it was converted directly into pentabromethan. The salt was distilled with an excess of baric hydrate, and the oily distillate absorbed by bromine water. A solid residue was left after evaporation of the excess of bromine, which melted at 53° when purified by crystallization from alcohol, and on analysis gave the required percentage of bromine.

0.0918 grm. of the substance gave 0.2041 grm. AgBr.

| | Calculated for $C_2HBr_5$. | Found. |
|---|---|---|
| Br | 94.12 | 94.61 |

Carbonic dioxide was evolved in this decomposition, and the retort residue contained baric bromide in large quantity. It may therefore be expressed by the following equation:

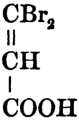
$$Ba(C_3HBr_4O_2)_2 = 2\,C_2HBr_3 + BaBr_3 + 2\,CO_2.$$

On standing with an alcoholic solution of potassic hydrate, a molecule of hydrobromic acid was eliminated from the acid with the formation of tribromacrylic acid, according to the equation:

$$C_3H_2Br_4O_2 + 2\,KOH = KC_3Br_3O_2 + KBr + H_2O.$$

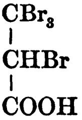
Tribromacrylic acid was recognized by its melting point, 118°, and by its crystalline form.

If the structure of $\beta$-dibromacrylic acid* is represented by the formula, —



$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

the bromine-addition product would have the form, —



$$\begin{array}{l} CBr_3 \\ | \\ CHBr \\ | \\ COOH \end{array}$$

The above statement concerning the behavior of $\beta$-dibromacrylic acid towards bromine, holds true with regard to chlorine. Although no action takes place at ordinary temperatures, when chlorine is passed through the melted acid the addition-product is formed without difficulty. The resulting dichlordibrompropionic acid will be submitted to further examination.

We have also tried the action of hydrobromic acid upon $\beta$-dibromacrylic acid, but as yet our results are as unsatisfactory as those of Fittig and Petri.† The product melted at about 53° and gave a percentage of bromine which showed that it contained much unaltered dibromacrylic acid. Nevertheless, by prolonged heating, we hope to obtain the tribrompropionic acid in a form sufficiently pure to enable us to study its properties.

Several attempts were made to obtain an addition-product by the action of bromine monochloride on brompropiolic acid. A substance was formed which melted quite constant at 110°–112°; but the results of analyses indicated that it was a mixture of the chlorine and bromine addition-products. In one experiment a product was obtained which melted at 102°–105°, and the percentage of bromine was very considerably increased. There is little doubt that the addition would take place, provided the bromine monochloride could be obtained in a state of purity under conditions necessary to form addition-products.

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* H. B. Hill, these Proceedings, Vol. XVII. p. 153.

† Ann. der Chem., cxcv. 73.

When brompropiolic acid is dissolved in chloroform saturated at 0° with chlorine, and allowed to stand for some time, the chlorine is absorbed with the formation of bromdichloracrylic acid.

## 2. ON THE DECOMPOSITION OF CHLORTRIBROMPROPIONIC ACID BY ALKALINE HYDRATES.

By C. F. Mabery.

In a previous paper by H. C. Weber and myself,* some experiments were mentioned in which we had attempted to determine the decomposition-products of chlortribrompropionic acid. Although our results were not entirely satisfactory, we were unable to verify them on account of the limited time at our disposal. Since the necessary material could be obtained without difficulty, it seemed worth while to define this reaction with greater precision. This work was undertaken by Mr. R. D. Wilson, who found that on prolonged heating with baric hydrate in aqueous solution chlortribrompropionic acid was completely decomposed, according to the equation, —

$$Ba(C_3HClBr_3O_2)_2 = 2\ C_2HClBr_2 + BaBr_2 + 2\ CO_2.$$

For identification the volatile product of the distillation was converted into chlortetrabromethan. It was caught in bromine water, the excess of bromine allowed to evaporate, and the oil which separated cooled to 0°. The solid thus obtained was purified by crystallization from alcohol, and its composition determined by analysis.

0.1556 grm. of the substance gave 0.3657 grm. AgBr + AgCl.

| | Calculated for $C_2HClBr_4$. | Found. |
|---|---|---|
| Cl + 4 Br | 93.42 | 93.30 |

Since this substance melted at 33°, it was probably identical with the chlortetrabromethan, melting point 32°–33°, obtained by Wallach and Bischof,† from the decomposition of β-dichloracrylic acid,

$$CCl_2 = CH - COOH.$$

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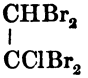
* These Proceedings, Vol. XVII. p. 209.

† Ann. der Chem., cciii. 89.

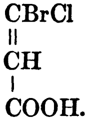
This acid gave chloracetylen, $CCl \equiv CH$, which by the addition of bromine formed chlortetrabromethan, —



$$\begin{array}{l}\mathrm{CHBr_2} \\ | \\ \mathrm{CClBr_2}\end{array}$$

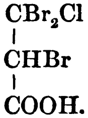
By the action of potassic hydrate in alcoholic solution upon chlortribrompropionic acid, the elements of hydrochloric acid were eliminated, with the formation in small quantity of tribromacrylic acid.

From the evident analogy between chlorbromacrylic acid, from which chlortribrompropionic was made, and β-dibromacrylic acid, the structure of chlorbromacrylic acid * is probably, —



$$\begin{array}{l}\mathrm{CBrCl} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{COOH.}\end{array}$$

Chlortribrompropionic acid would then have the form, —



$$\begin{array}{l}\mathrm{CBr_2Cl} \\ | \\ \mathrm{CHBr} \\ | \\ \mathrm{COOH.}\end{array}$$

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* H. B. Hill, these Proceedings, Vol. XVII. p. 153.